

# The Effect of Teflon Emulsion on Hydrogen Electrode Properties and Performance in Nickel-Hydrogen Cells

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## The Effect of Teflon Emulsion on Hydrogen Electrode Properties and Performance in Nickel-Hydrogen Cells

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The traditional T30 Teflon emulsion used in nickel-hydrogen battery cells is being phased out due to EPA concerns with two of its minority components. This presentation reviews work done by The Aerospace Corporation to better understand the relationship between the properties of the hydrogen electrode affected by the Teflon emulsion and cell performance. Special cycling tests have been derived to selectively stress the hydrogen electrode with minimum stress to the nickel electrode. Results from these tests performed on cells constructed with T30 and an alternative emulsion, TE3859, are presented.



## Concern

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- T30, the Teflon emulsion used in the manufacture of hydrogen electrodes used in nickel-hydrogen cells, will soon no longer be available
  - PFOA (perfluorooctanoic acid) and Triton X-100 surfactant is being phased out in North America and Europe due to environmental concerns
  - T30, an aqueous solution of Teflon containing both of these compounds, was removed from the commercial market in 2007
  - Teflon emulsions have a short shelf life due to Teflon particle settling and coagulation

Last year, Dupont announced that it would no longer produce a type of Teflon emulsion known as T30 due to a world-wide ban on the perfluorooctanoic acid (PFOA) content of its delivered Teflon products. This was grave news for many users of nickel-hydrogen satellite batteries, the battery of choice for high reliability and high performance military and commercial satellites, because Teflon is a vital component of the hydrogen electrode used in cells, and alternative Teflon emulsions had not been previously explored.

T30 is a type of aqueous Teflon emulsion that contains small amounts of PFOA and Triton X-100 surfactant, both of which are being eliminated due to environmental concerns. Replacement emulsions offered by Dupont contained different minority species, and the effect of these components on cell performance and cell life is not known.

Stockpiling existing T30 emulsions for future battery buys was not a viable near-term option because its shelf life is typically only on the order of 6-12 months. With time, the Teflon particles in these emulsions coagulate, changing the characteristics of the finished hydrogen electrodes.

## Approach

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- Establish a better understanding of the links between the properties of the Teflon emulsion, hydrogen electrode and cell performance
  - Materials characterization
  - Electrode characterization
  - Cell performance
- Put in place tools and methods of evaluation for more quickly evaluating candidate replacement emulsions when T30 is no longer available
  - TE3859, now in-use commercially as a replacement for T30, is expected to be removed from production by 2013 due to further restrictions on the use of PFOA during manufacturing



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Although T30 will be available in the near term, by 2013, an alternative Teflon emulsion will be needed to continue the production of nickel-hydrogen cells. The present approach by the Energy Technology Department of The Aerospace Corporation to assist with this effort is to establish a better understanding of the link between the properties of the Teflon emulsion and hydrogen electrode to cell performance and life.

To date, characterization testing of the emulsions and hydrogen electrodes has been initiated to provide a baseline for the T30-based electrodes and to understand the allowable variation in properties. Stress tests at the plate and cell level are being developed to understand the wear-out modes for the hydrogen electrode.

The goal of this effort is to put in place tools and test methodology for more quickly evaluating candidate replacement emulsions. Although an alternative emulsion, TE3859, is in-use commercially as a replacement for T30, TE3859 is not expected to be available after 2013 due to further restrictions on the use of PFOA during manufacturing. All the same, TE3859 is being used in the present test effort to understand what differences are likely to arise once a long-term replacement emulsion is identified.



## Historical Development of the Hydrogen Electrode

- Hydrogen electrodes composed of Teflon were developed for alkaline fuel cells in the 1960s
- When nickel-hydrogen cells were proposed as an alternative to nickel-cadmium cells for satellites, the same hydrogen electrode was tested and implemented
- Hydrogen electrode composition
  - Nickel screen current collector
  - GoreTex membrane on backside to retard water loss
  - Pt/Teflon active material to reversibly catalyze the conversion of water to hydroxide and hydrogen
- Hydrogen electrode processing parameters were optimized to provide the best performance in fuel cells

Hydrogen gas diffusion electrodes were developed in the 1960s for low temperature alkaline fuel cells employing aqueous electrolytes. They rely on the hydrophobic nature of the Teflon phase to prevent the electrolyte from completely flooding the pores in the electrode, permitting the diffusion of hydrogen and oxygen gas in and out of the electrode. The Teflon phase was utilized both to help stabilize the gas interface as well as provide a binder for the Pt (platinum) black electrocatalyst particles. NASA later optimized the hydrogen electrode for alkaline fuel cell applications after they discovered that flooding could be reduced in their anodes by optimizing the sintering temperature.

Nickel-hydrogen cells succeed because the spontaneous reaction rate between hydrogen gas and  $\text{NiOOH}_2$ , which causes self discharge in cells, is relatively slow. Hydrogen electrodes already developed from fuel cells were easily adopted for the  $\text{NiOOH-H}_2$  couple and little further development was required for their use in nickel-hydrogen cells.



## Operation of the Hydrogen Electrode

- Charge  

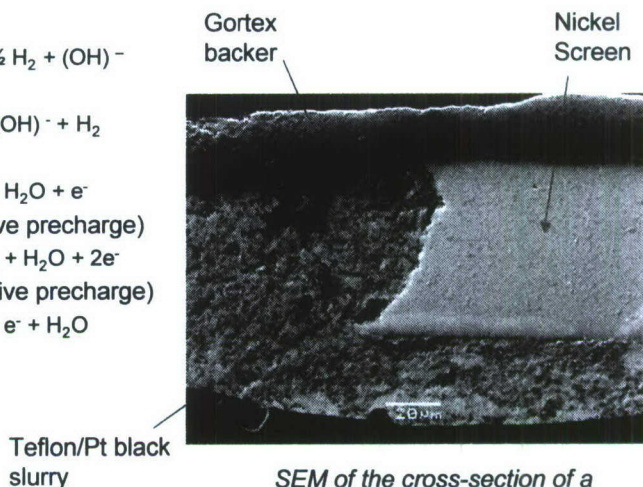
$$\text{H}_2\text{O} + \text{e}^- \rightarrow \frac{1}{2} \text{H}_2 + (\text{OH})^-$$
- Overcharge  

$$2\text{H}_2\text{O} + 2\text{e}^- \rightarrow 2(\text{OH})^- + \text{H}_2$$
- Discharge  

$$\frac{1}{2} \text{H}_2 + (\text{OH})^- \rightarrow \text{H}_2\text{O} + \text{e}^-$$
- Reversal (positive precharge)  

$$2(\text{OH})^- \rightarrow \frac{1}{2} \text{O}_2 + \text{H}_2\text{O} + 2\text{e}^-$$
- Reversal (negative precharge)  

$$\frac{1}{2} \text{H}_2 + (\text{OH})^- \rightarrow \text{e}^- + \text{H}_2\text{O}$$



SEM of the cross-section of a hydrogen electrode

The hydrogen electrode acts as a catalyst to reversibly react water to form hydrogen and hydroxide. The backside of the active material is coated with a porous, hydrophobic Gortex screen to allow gas access but prevent water and electrolyte loss from the electrode. A nickel screen is embedded in the active material to transport electrons to and from the reaction. The active material consists of a porous suspension platinum black particles and Teflon. The platinum black particles are hydrophilic and the Teflon is hydrophobic. While the hydrogen electrode requires some hydrophilic properties in the particles to facilitate reactions at the liquid-catalyst-gas interface, the hydrophobic nature of the dispersed Teflon phases is critical to prevent electrode flooding and shutdown of the chemical reaction.

In the right proportion and distribution, this two-phase material stabilizes a three phase, solid-liquid-gas interface, for supporting the reaction of the gaseous hydrogen and liquid electrolyte.

The SEM (scanning electron microscopy) image of a cross section of a hydrogen electrode shows the relative amount of Gortex backing, current collector, and active material present in a typical hydrogen electrode.

### Reported Failure Modes Associated with Hydrogen Electrodes

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- Alkaline Fuel Cell Applications
  - Excessive hydrophilic nature – flooding
  - Excessive hydrophobic nature – insufficient wetting
  - Flooding due to water vapor accumulation
    - More commonly a concern at higher temperatures
  - Recrystallization of Pt particles over life
    - Lowers reactivity and catalyst surface area
  - Oxidation and dissolution of platinum
  - Carbon dioxide poisoning - usually from impure reactant gases
  - Silicate build-up from asbestos wicks
- Battery Applications
  - Shorting due to Pt particle dislocation

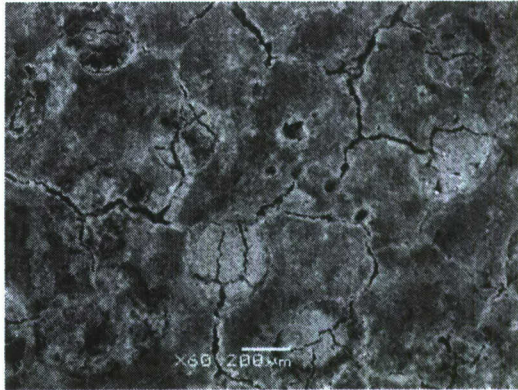
In alkaline fuel cells, Teflon-supported catalyst electrodes are used both for the oxygen and hydrogen electrodes. Wear-out tends to be highest in the oxygen electrode where overpotentials are much higher than the hydrogen electrode (and much higher than in the hydrogen electrode used in nickel-hydrogen cells). Failure modes previously reported in Teflon catalyst oxygen electrodes include flooding, insufficient wetting, water vapor accumulation, recrystallization of Pt particles, and oxidation and dissolution of platinum particles. These effects have not generally been found in nickel-hydrogen cells largely due to the lower operating temperatures and lower degree of polarization. Furthermore, other problems such as carbon dioxide poisoning and silicates accumulation are absent in nickel-hydrogen cells.

Failure mechanisms relating specifically to the hydrogen electrode in nickel-hydrogen cells are few and changes in the nickel electrode are usually responsible for the losses in cell performance. However, Pt particle adhesion has been cause for concern, and dislodged Pt particles could provide a shorting path between plates.



## Structure of the Hydrogen Electrode

- Materials Parameters of Interest
  - Conductivity
  - Surface Area
  - Pore size distribution
  - Density
  - KOH retention
  - Gas permeability
  - Cracking
  - Adhesion of the active material
  - Phase distribution of Pt and Teflon



*SEM Image of the top surface of a hydrogen electrode*

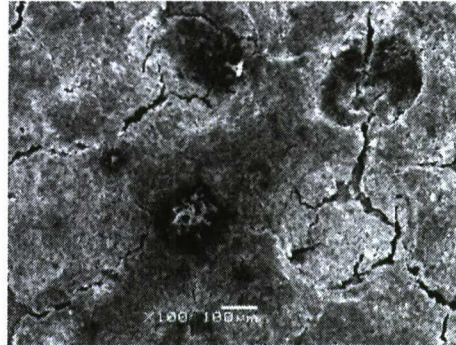
SEM analysis of finished hydrogen electrodes found a surprisingly complex microstructure consisting of cracks and surface craters responsible for the porous structure of the electrode. It is believed that this microstructure is necessary for providing sufficient surface area for the reactions to occur as well as to provide sufficient capillary action to draw the electrolyte into the middle of the electrode.

Good electrical conductivity and the ability to easily move reactants and products into and out of the hydrogen electrode are necessary for satisfactory cell performance. For that reason, the variables of interest in the finished hydrogen electrode include conductivity, surface area, pore size distribution, KOH (potassium hydroxide) retention, gas permeability, cracking characteristics, adhesion of the active material, and phase distribution of Pt and Teflon particles.



## Processing Variables of Interest

- Mechanism for creating pores and surface area considered important for electrode performance...
  - Impact of the surfactant type
  - Impact of sintering temperature
  - Impact of other processing variables such as cooling rates, pressure levels, slurry composition
- ....however, how much change can be accommodated without affecting performance or life is not known



*SEM Image of the top surface of a hydrogen electrode with residue left in surface crater*

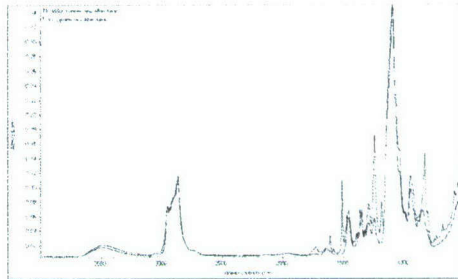
The manner in which the water, surfactants and other additives leave the material to produce the final surface structure are of key interest. In the image above, a residual compound is still evident in the center of a surface crater.

Because much of the market for Teflon emulsions come from sectors interested in very smooth Teflon coatings in their final products, there is high demand for replacement emulsions that produce less cracking after sintering. For this reason, it is expected that the changes in electrode surface structure, pore size distribution, and wetting of the Pt black particles should be carefully studied to identify suitable candidate Teflon emulsions to replace T30.

Furthermore, the effect of processing variables such as sintering temperature, pressure levels, slurry composition, etc. on the final product needs to be better understood. It is possible that adjustments in processing variables might reduce the impact of the newer emulsions on the morphology of the finished hydrogen electrode.

## Comparison of T30 with TE3859 Replacement Emulsions

- Analysis of Trace Components
  - FTIR analysis confirmed that T-30 contained volatiles consisting of phenol ethoxylates; octyl, nonyl and decyl phenol ethoxylates
  - FTIR analysis confirmed that TE3859 contained polyethylene glycol monomethyl ether
- Different volatility of new surfactants on likely to affect final surface area and pore size distribution for the same sintering temperatures
- Effect of different class of surfactants on electrode life is unknown
  - Ability to wash residues from electrodes also unknown



*FT-IR spectra of the T-30 and TE-3859 residues of the centrifuged supernatant heated to 120°C*

Analysis of the Teflon emulsion by GC-MS (gas chromatography mass spectroscopy) and FTIR (Fourier Transform Infra-Red analysis) can provide the identity of the minor components so that the changes in volatilization temperature can be determined. T30 and TE3859 were analyzed by these methods to identify the minor compounds in each.

The impact of the residues in these emulsions on hydrogen electrode life is unknown. At one time, there was concern regarding the effect of T30 residues electrodes in hydrogen electrodes for military missions which drove a requirement for washing finished electrodes in trichloroethylene and ethanol. However, this practice was later discontinued.

As a side note, the aging characteristics of T30 are also being studied as part of this effort with these methods. Decomposition products hexanoic, pentanoic, and nonanoic, and hexadecanoic acids have been identified by GC-MS in emulsions stored in excess of 12 months at room temperature.



### Plate Characterization for T30 and TE3958 Electrodes

- In 2006, Aerospace sampled 24 electrode plates, 50% produced with T30 and 50% produced with TE3859.
- Tests included:
  - Density, thickness
  - Adhesion, surface appearance
  - KOH wettability, gas permeability, bubble pressure
  - Pt solubility, hot KOH exposure
  - Inorganic and organic contaminants
  - SEM analysis for pore, Pt particle, Teflon distribution, and cracking characteristics
  - Oxygen and hydrogen overpotential measurements



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In 2006, Aerospace sampled 24 electrode plates made from T30 and TE3859 that were produced at the same time using the same process parameters. To determine whether the porous volume, pore size, and phase distribution had changed, measurements for the plate thickness, density, and KOH wettability were taken. Cross sections of plates were studied by SEM to sample pore size, Pt particle and Teflon distribution, and cracking patterns. Gas permeability was measured from the flow rate across electrode samples, and bubble pressure determined by applying a vacuum on one side of the electrode while the other side immersed in water. Pt solubility was measured by weighing following a 0.2mA/cm<sup>2</sup> oxidation current applied for 24 hours in 31% KOH. Hot KOH exposure consisted of a 24-hour exposure test in a sealed bomb at 120°C. Elemental contaminants were analyzed by ICP-MS, and organic contaminants were determined by GC-MS analysis of the nonvolatile residue obtained by extraction with hexane and acetone.

Overpotential testing was done in hydrogen and oxygen gas using test cells consisting of a gas screen, two-layer Zircar separator, Pt catalyst reference electrode, and nickel counter electrode. Components were compressed between plexiglass plates and activated with 31% KOH and drained prior to installation in a stainless steel vessel. Charge and discharge rates were varied from 0.2 to 50 mA/cm<sup>2</sup> at ambient temperature.



## Results of Plate Characterization for T30 and TE3958

- TE3859 electrodes were thinner and more dense, less wettable with KOH and had smoother surface
  - 20 – 50% less KOH held within pores
  - Less internal pore and void volume
  - Loss of much of the larger pores compared to T30 electrodes
  - Loss of much of the macroscopic cracking compared to T30 electrodes
  - Slightly more organic residuals
- Slightly poorer Pt catalyst adhesion in TE3859 electrodes
  - Adhesion degraded slightly more by hot KOH exposure
- Small changes in averaged charge and discharge voltages
  - Higher H<sub>2</sub> evolution (recharge) voltage for TE-3859 (about 10mV at C/2)
  - Similar H<sub>2</sub> recombination (discharge) voltages
  - Lower O<sub>2</sub> recombination potential for TE-3859 (about 20mV at C/2)
  - Higher O<sub>2</sub> evolution potential for TE-3859 (about 10mV at C/2)

Initial comparison of the electrodes provided found higher densities and lower internal pore volume in the electrodes made with TE3859. Due to this reduced pore volume, there was lower total KOH electrolyte retained in the electrode and it appeared that many of the larger sized pores were lacking compared to T30.

The platinum particle adhesion was relatively lower in the TE3859 as measured by the amount of material lost due to gentle surface scraping and pulling adhesive tape from the surface. However, the losses seen were within prior experience for earlier studies on T30 electrodes.

On average, electrochemical differences measured by the gaseous evolution and recombination voltages were small and generally within sample-to-sample variation of electrodes using the same type of emulsion.

## Impact of Normal Processing Variables

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- Difficult to interpret electrode test results because the normal variation of these parameters for T30 were unknown
  - Aerospace then studied 10 samples each of T30 and TE3859 electrodes where the post-sintering cool-down was varied between the allowable minimum and maximum rates
- Tests performed included:
  - Density, thickness, adhesion to substrate, surface appearance
  - KOH wettability and gas permeability
- Results found:
  - Cooling rate affected electrode density and active material adhesion
  - Range found overlapped the range seen in the prior T30 & TE3859 tests
  - Gas permeability affected by degree of compression of the Gortex layer



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The results of the 24-sample study were difficult to interpret due to the lack of a baseline for expectable variation of those parameters due to processing variables. Therefore, it was decided to vary a single processing variable, the post-sintering cooling rate, to determine how that variable alone would affect electrode density, KOH retention, adhesion, surface appearance, and gas permeability.

Results from electrodes using both T30 and TE3859 emulsions found that the cooling rate had a marked impact on both electrode density and active material adhesion that was of the same magnitude as the variation found in the prior study.

### Cell Testing with T30 and TE3859

- Four 90Ah cells received from EP for evaluation
  - RNH90, double zircar separator, wall wick, 31% KOH, and strain gages
  - Two made with T30 (cells 1, 4) and two with TE3859 (cells 2 & 3)
- Capacity measured at -10, 0, 10°C
  - Charge at C/10 (9A) for 16 hours followed by a C/2 (45A) discharge to 1.0V
- Voltages were slightly higher in TE3859 cells during charge and discharge

	T30 (Cell 1)	T30 (Cell 4)	TE3859 (Cell 2)	TE3859 (Cell 3)
Capacity (Ah)				
-10°C	104.2	105.5	105.4	104.8
0°C	106.8	107.0	107.3	107.5
10°C	98.3	97.9	98.4	98.4
EOC Voltage				
-10°C	1.604	1.603	1.606	1.605
0°C	1.561	1.560	1.561	1.562
10°C	1.519	1.519	1.520	1.520

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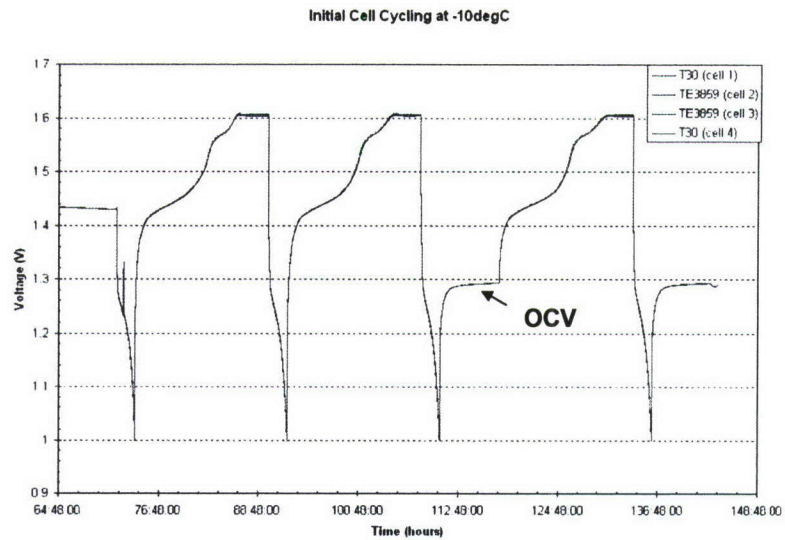
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With the help of a program office and Eagle-Picher, two cells containing hydrogen electrodes made with T30 and two cells containing TE3859 electrodes were obtained. All four 90Ah cells were made in 2006 and were of the same design, using a double zircar separator, catalyzed wall wick, and 31% KOH electrolyte. Each cell was equipped with a calibrated strain gage for monitoring cell pressure.

Standard capacity measurements to 1.0V at a C/2 discharge rate following a C/10 charge for 16 hours at -10, 0, and 10°C were nominal and no significant difference was seen between cells. End of charge voltages following the 16 hour C/10 charge were slightly higher in the cells containing TE3859 electrodes.



## Initial Capacity Cycling of Four Cells at -10°C: Voltage



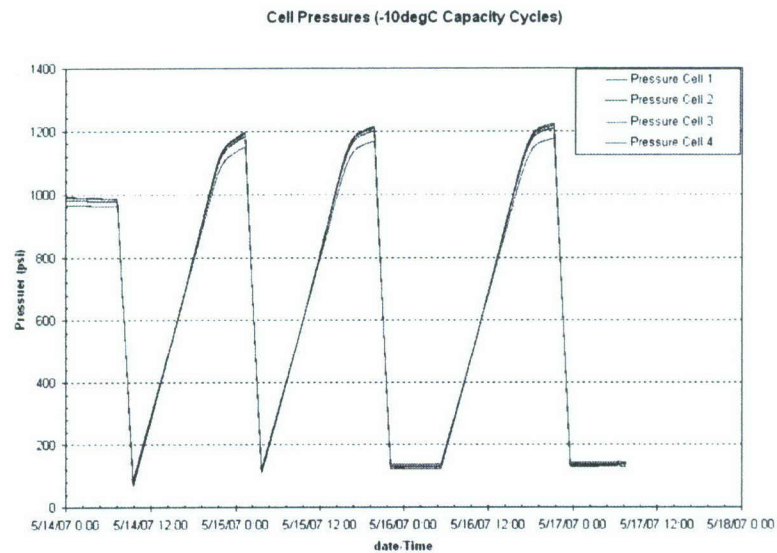
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The graph shows the voltage trace of all four cells during initial capacity cycling at -10°C.

## Initial Capacity Cycling of Four Cells at -10°C: Pressure



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The graph shows the change in pressure for all four cells during the initial capacity cycling at -10°C shown on the previous slide. Pressure differences between cells are small.



### Cell-Level Testing of Cells made with T30 and TE3859

- Problem: How to test  $\text{NiH}_2$  cells to best compare the capability of the different hydrogen electrodes?
  - The nickel electrode is usually the life-limiting electrode when cycling  $\text{NiH}_2$  cells
- Typically, life tests and stress tests defined for  $\text{NiH}_2$  cells are designed to stress the nickel electrode
  - Higher depth of discharge
  - Increased temperature
  - Increased amount or rate of overcharge
  - Increased frequency of cycles (throughput)
- Stress factors appropriate to the  $\text{H}_2$  electrode were proposed
  - Increased rates for charge and discharge
  - Reduced temperatures to evaluate liquid and gas transport processes
  - Overcharge to evaluate  $\text{O}_2$  recombination tolerance



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To maximize the sensitivity to possible differences in the hydrogen electrodes, standard nickel-hydrogen stress cycling tests were avoided because those are known to encourage wear-out modes of the nickel-electrode. The parameters relating to faster nickel hydrogen electrode deterioration include high depths of discharge, high temperatures, high amounts or rates of overcharge, and high through-put. Where possible, these parameters were minimized.

Instead, stress factors believed to better target the hydrogen were chosen including increased rates for charge and discharge, reduced temperatures to encourage concentration polarization due to lower diffusivities of reactants and products, and overcharge to increase oxygen gas exposure and recombination tolerance.

## Hydrogen Electrode Stress Test Cycle

- Low temperature operation:  $-10^{\circ}\text{C}$  at end of charge
  - Enables operation with minimal overcharge to stress the nickel electrodes
  - Worst case for transport processes
  - Relatively abrupt onset for oxygen evolution at full charge
- 90-minute cycle profile
  - 30 minutes discharge, 60 minutes recharge
- 40% DOD with periodic high rate discharge pulses
  - Three cycles of 8 minutes discharge at 0.5C followed by 2 minutes at 2C for a 40 DOD
  - High rate pulses expected to stress the  $\text{H}_2$  electrode transport capabilities
  - Pulse periodicity expected to allow  $\text{H}_2$  pressure dependence to be studied
- High peak recharge rate (C-rate)
  - Current taper at a peak cell charge voltage limit
  - One set of cells run at 1.02 RCF, other set at a 1.04 RCF target (1.03 – 1.05 actual)
    - Lower RCF cells go to open circuit conditions while the second set of cells obtain their higher RCF during the 60 minute charge



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The four cells were assembled into a single pack and mounted in a base-plate with strain gages on each cell and near each cell on four positions on the block. Cell voltages, pressures, and temperatures are individually monitored. Cells are connected in series to a single power supply and electronic load bank with bypass circuitry for applying different end of charge voltages and recharge ratios to each pair of cells.

To maximize stress to the hydrogen electrode with minimal impacts to the nickel electrodes, all cell cycling is done with an end-of-charge temperature of  $-10^{\circ}\text{C}$ . A 90 minute charge/discharge cycle was chosen with a moderate DOD of 40%. High current discharges of up to 2C are periodically applied to stress the transport processes in the hydrogen electrode. A peak charge rate of 90A (C) is used with a current taper as cells reach their recharge fraction (RCF). The four cells are split into two pairs (each pair with a T30 and a TE3859 cell) and run at two different RCF, one pair at 1.02 and the other at 1.03 – 1.05. To attain the higher RCF, the maximum allowed voltage on the second pair of cells is set at a higher level.



## P/F Criteria and Parameters Trended

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- Tests will run until cell voltage falls below 0.7 V during 2C discharge or 1.0 V at 0.5C
  - To date, over 1880 cycles had been applied
- Parameters trended for possible sensitivity to the type of emulsion used in the hydrogen electrodes
  - Voltages signatures during charge and discharge
  - EOCV and EODV
  - Current taper
  - Recharge ratios (RCF)
  - Thermal signatures
  - Pressure signatures



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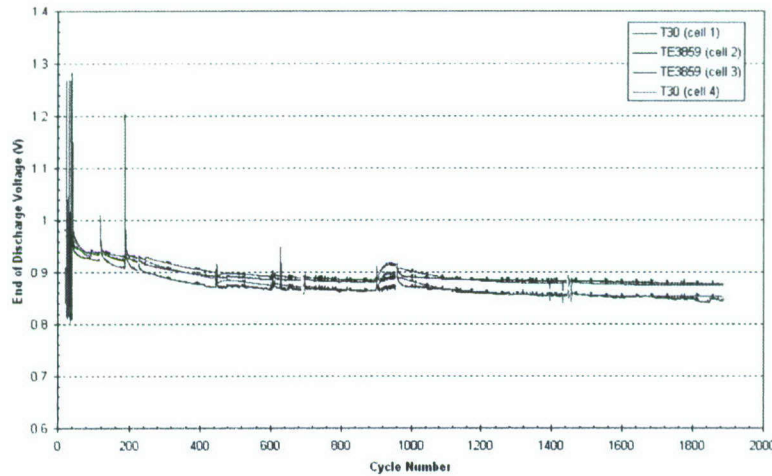
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The goal of the tests is to cycle cells until cell voltage falls below 0.7V at the 2C discharge rate or 1.0V at the 0.5C rate. Also, the following parameters are being evaluated for possible differences due to changes in hydrogen electrode performance: voltage signatures, end-of-charge (EOCV) and end-of-discharge voltages (EODV), recharge ratios, changes in the taper current, thermal signatures, and pressure signatures.

As of Oct. 2007, over 1880 cycles had been applied to the four cells without failing the defined voltage limits.

## Stress Test Results to Date: End of Discharge Voltage

EODV as a function of Cycle Number  
(measured at the maximum pulse discharge rate)



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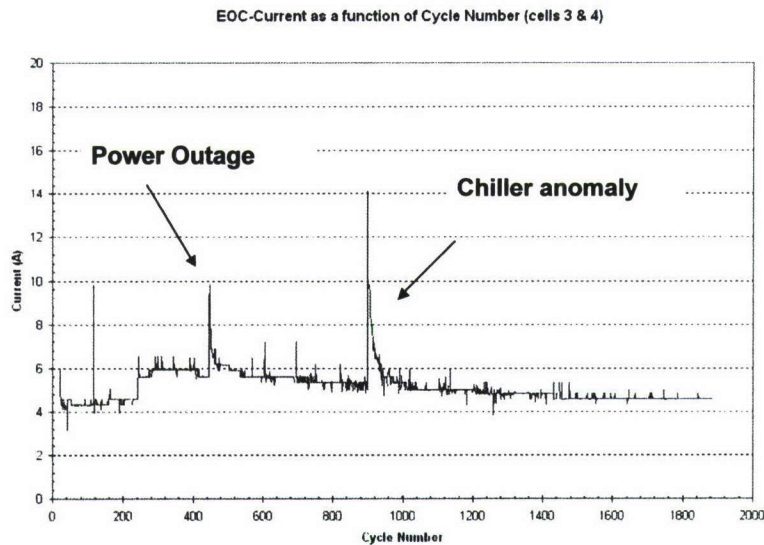
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At the beginning of life, the voltage at the end of discharge was lower in the cells containing the T30 electrodes. However, the loss in voltage at the end of discharge to date has also been higher in the T30 electrodes as shown in this graph. Furthermore, the rate of loss appears to be about the same for both T30 cells despite the higher RCF in cell 4.



## Stress Test Results to Date: Current Taper (cells 3 & 4)



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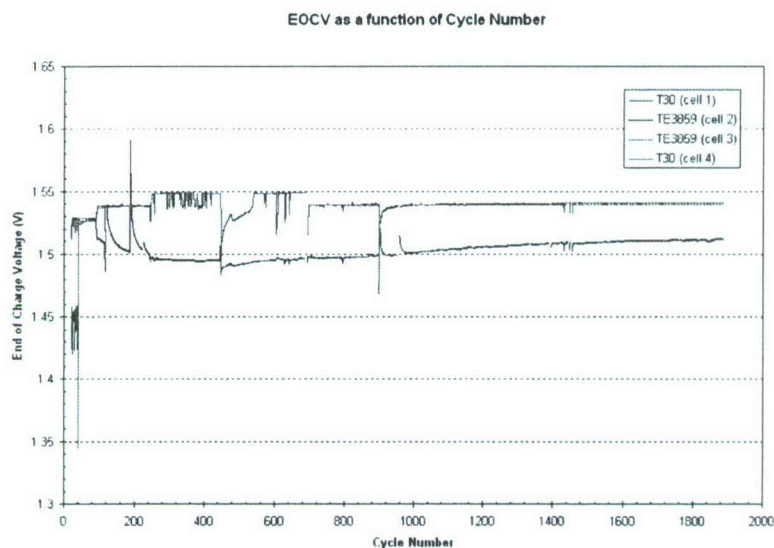
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The current taper for cells 3 & 4, which are charged to 1.03 – 1.05 RCF is shown as a function of charge cycle. The drop off in charge current is consistent with the drop in RCF over time (shown in a later slide).

An overnight power outage occurred at cycle 446, and cells warmed up to 23°C before the test was re-started. At cycle 899, a chiller anomaly occurred resulting in a current shutdown to the cells. However, a fan inside the thermal shielding remained on and inadvertently heated the cells to 45°C.

## Stress Test Results to Date: End of Charge Voltage



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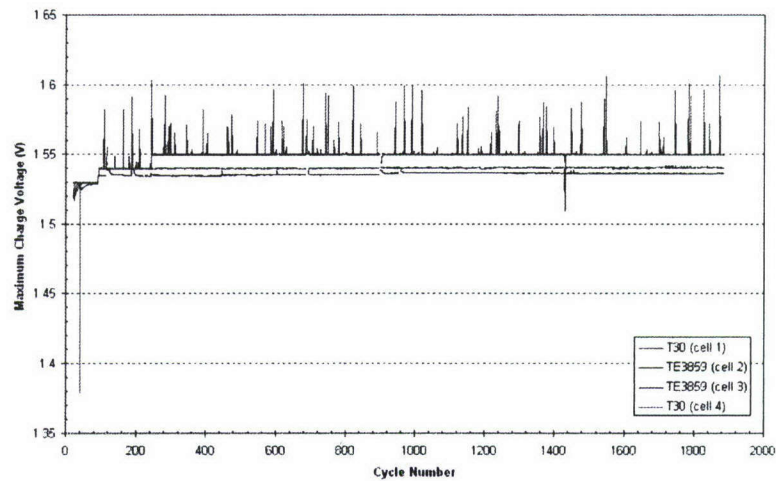
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The end of charge voltage for cells 1 & 2, which are charged to the lower RCF of 1.02 are rising. This trend is due, in part, to their lower amount of time left in the open circuit condition during the previous charge cycle.

## Stress Test Results to Date: Max Charge Voltage prior to Taper

Maximum Charge Voltage as a function of Cycle Number



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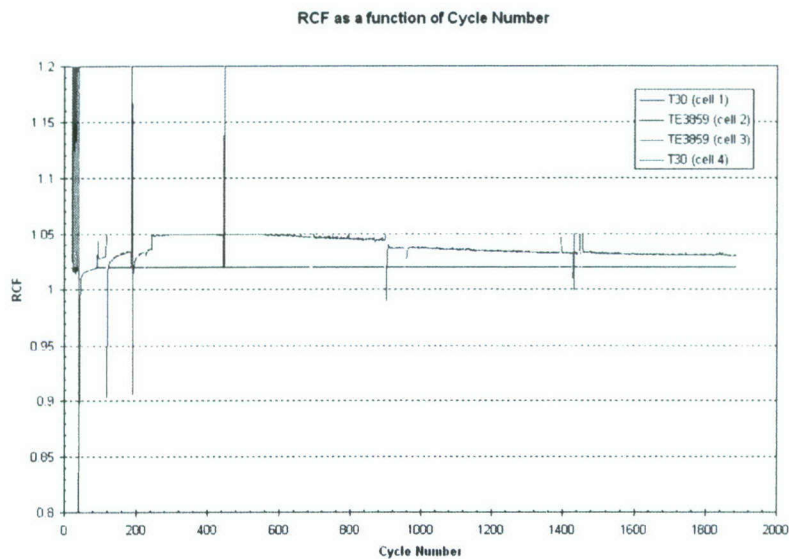
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The maximum charge voltage has not been changed for the majority of testing so far.



## Stress Test Results to Date: Recharge Fraction (RCF)



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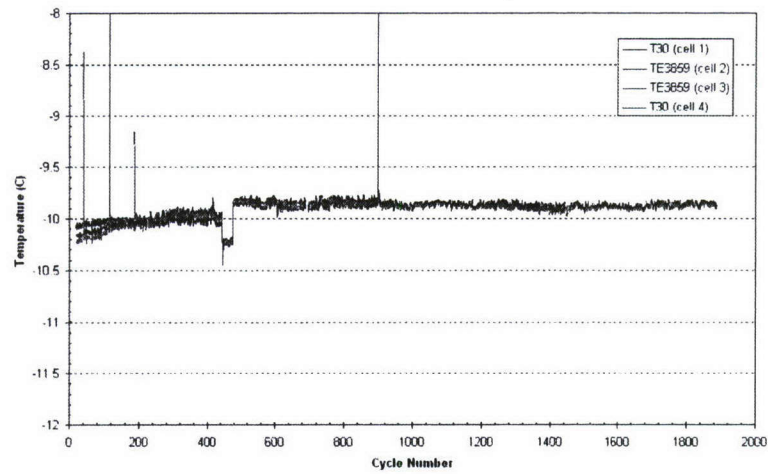
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However, the RCF for the cells set at the higher charge voltage limit are dropping. The end of charge voltage for those cells will be increased to accomplish the 1.05 RCF in later cycles.

## Stress Test Results to Date: End of Charge Temperature

End of Charge Temperature as a function of Cycle Number



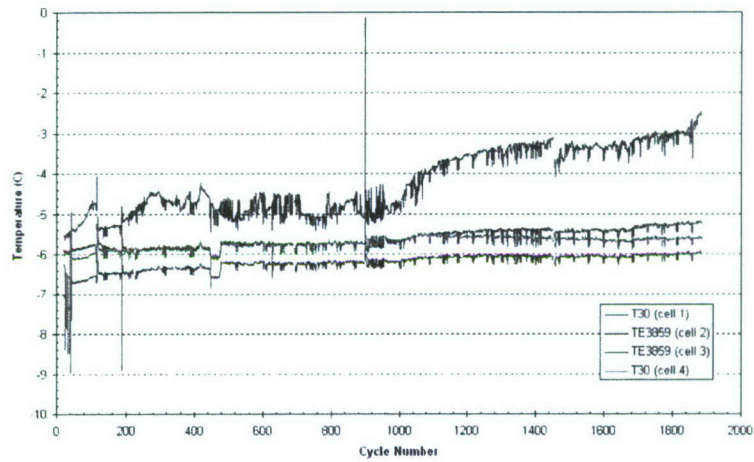
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No change has been seen in the end of charge temperature to date.

## Stress Test Results to Date: End of Discharge Temperature

End of Discharge Temperature as a function of Cycle Number

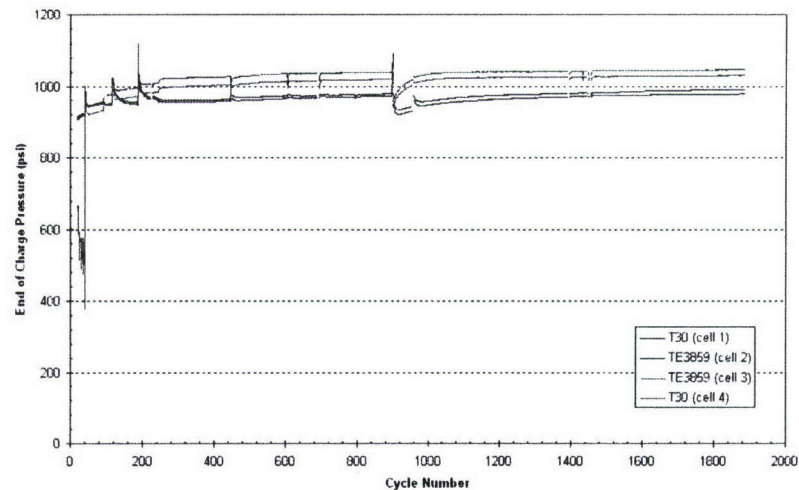


However, the end of discharge temperature is consistently creeping up in cell 1. It is not known why this is occurring and is under evaluation.



## Stress Test Results to Date: End of Charge Pressure

End of Charge Pressure as a function of Cycle Number



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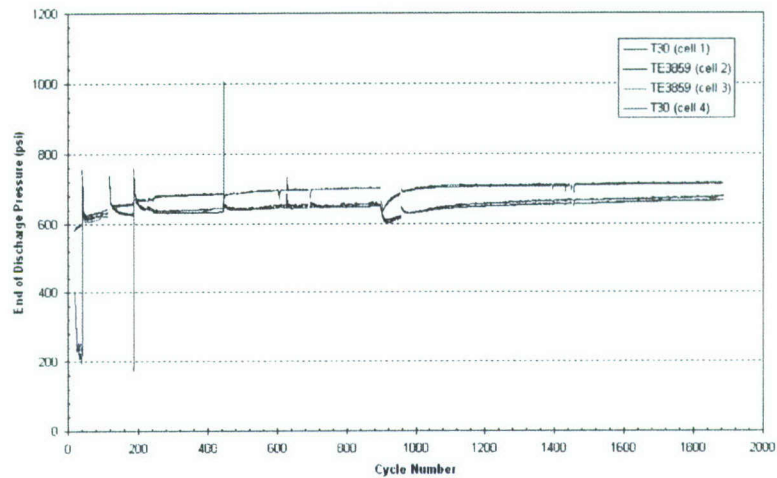
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End of charge pressures have shown a small increase with 40% DOD cycling.

## Stress Test Results to Date: End of Discharge Pressure

End of Discharge Pressure as a function of Cycle Number



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End of discharge pressures have also shown a small increase with cycling.

### Summary of Findings to Date

- Differences in surfactants used in electrodes expected to impact microstructure of electrodes produced due to differences in volatility, however, processing variables may have as strong of an impact
  - Expect to need to vary some processing parameters for follow-on replacement emulsion for T30
  - Need to develop the allowable range for critical parameters based on existing T30 production lots
- Different Teflon emulsions expected to show small impacts in charge and discharge voltages
- Low temperature, high pulse cycling of cells containing T30 electrodes and other cells containing TE3859 electrodes are presently showing greater end-of-discharge voltage losses in the cells containing the T30 electrodes
  - About 1850 cycles applied so far



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To date, plate-level and cell level tests have been run and are in the process of being run on hydrogen electrodes containing T30 and TE3859. Although plate-level tests found higher densities and reduced porous volume and average pore size in the TE3859 electrodes, similar changes could be produced in T30 electrode by varying production parameters within their allowed limits.

It is expected that the eventual replacement emulsion for T30 will require some process refinement to produce the same material properties found in T30 electrodes, and there is a need to continue to study the T30 electrodes made to date to determine the allowable range for properties such as surface area, pore size, pore size distribution, KOH retention, etc.

Cell-level tests of cells containing electrodes made of either T30 or TE3859 show a slightly higher end-of-charge voltage in the TE3859 cells at beginning of life. However, testing to a 90-minute, low temperature, high discharge rate profile has produced more end-of-discharge voltage loss in the T30 cells for the 1850 cycles applied to date.



#### Next Directions

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- Continue four-cell low temperature cycling tests
- Continue baseline effort for existing T30 electrodes
- Study variation of processing parameter on hydrogen electrode material characteristics
  - Surface area, porosity
  - Hydrophobicity
  - KOH retention
- Study variation of processing parameter on hydrogen electrode material characteristics
  - Plate-level stress tests
- Evaluate candidate replacement emulsions when they become available



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The Aerospace Corporation plans to continue work in the study of the impact of materials properties of the Teflon emulsion on plate and cell performance in FY08. The cell tests in progress will be monitored for changes that can be linked to differences in the type of Teflon emulsion used. Testing of existing T30 electrodes will be continued to better baseline material properties and to understand the impact of processing variables on the finished product. The hydrogen electrodes from cells taken off life-test at Crane will be studied to document the material changes and deterioration that occurs in the hydrogen electrode. Electrical evaluation and stress tests for evaluating hydrogen electrodes will be developed.

The understanding and tools gained from this multi-year research effort will be utilized to evaluate candidate Teflon emulsions compliant with future EPA requirements when they become available.

## Acknowledgments

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- The author is grateful for the assistance and contributions of the following personnel:
  - The Aerospace Corporation: Lindsay Berger, Boyd Carter, Myriam Easton, Tom Giants, Warren Hwang, Michael Quinzio, Larry Thaller, and Gloria To
  - Boeing: Ken Jennings
  - Eagle-Picher: Jeff Dermott
- The Aerospace Corporation is gratefully acknowledged for supporting this work as part of the Aerospace Mission Oriented Investigation and Experimentation (MOIE) program.
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The authors are grateful for the technical assistance and contributions of their Aerospace colleagues for these studies. Dr. Larry Thaller has been instrumental in developing the low temperature pulse stress test used to characterize the cells with different Teflon emulsions, and in providing the background of how the hydrogen electrode was developed for fuel cell applications. Dr. Tom Giants and Ms. Myriam Easton have guided the Teflon emulsion characterization work and have provided valuable insight in understanding the implications of the changes seen in the GC-MS and FTIR data.

The author is grateful to Mr. Jeff Dermott for providing Teflon emulsions, hydrogen electrodes and test cells for this effort, and Mr. Ken Jennings for providing Teflon emulsions for study.

This work has been funded by The Aerospace Corporation Mission Oriented Investigation and Experimentation program. The goal of this program is to provide analysis and data across programs to better assist program offices in achieving mission success.

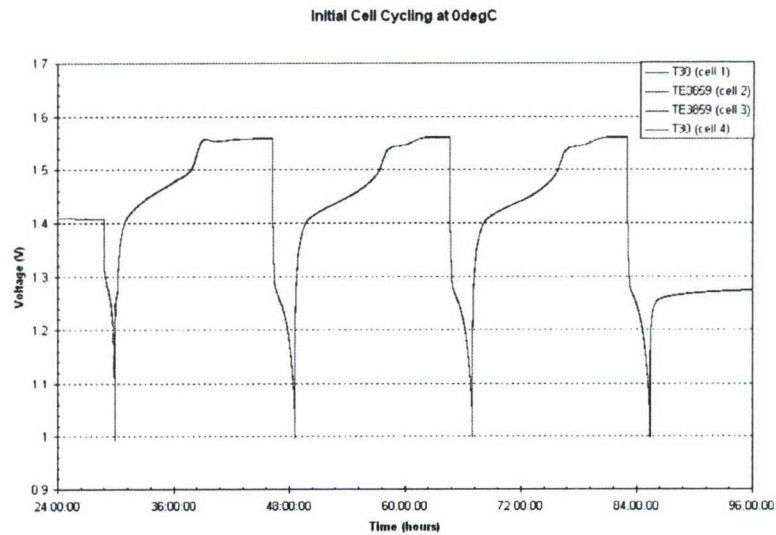
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## Additional Data

The follow slides provide additional data from the four cell tests in progress.



## Initial Capacity Cycling of Four Cells at 0°C



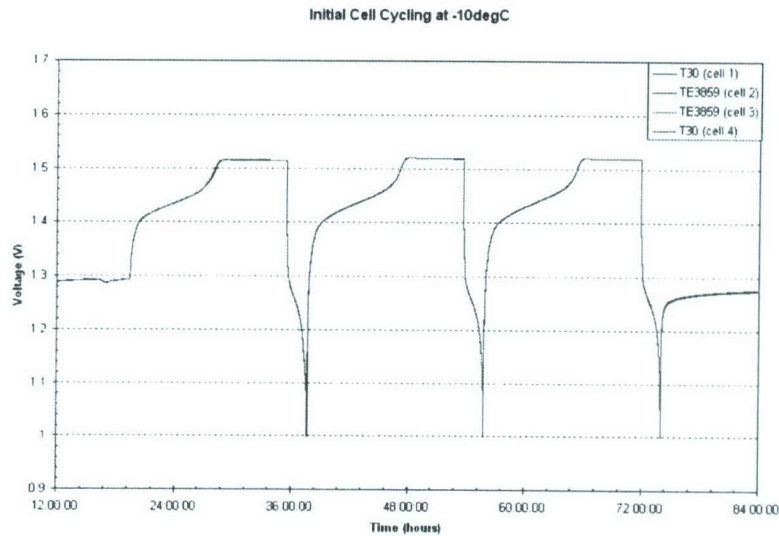
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This graph shows the voltage changes of the four cells during capacity testing at 0°C at beginning of life. All four traces lie on top of each other for the resolution of this graph.

## Initial Capacity Cycling of Four Cells at 10°C



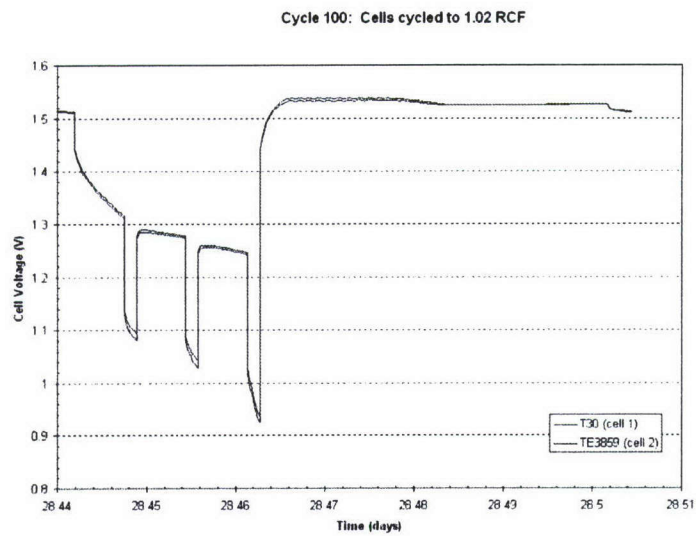
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This graph shows the voltage changes of the four cells during capacity testing at 10°C at beginning of life. All four traces lie on top of each other for the resolution of this graph.

## Cycle 100 Curves for 1.02 RCF



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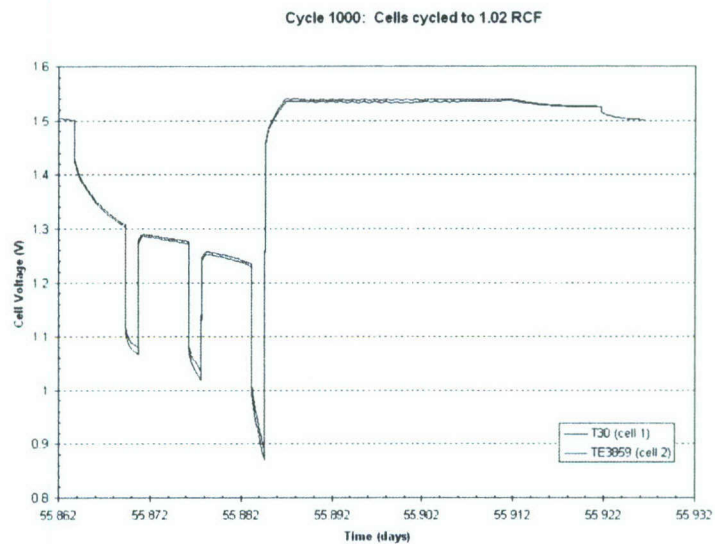
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The graph shows the voltage change in the two cells tested to a 1.02 RCF at cycle 100. Cell 1 (blue) contains the T30 electrodes and Cell 2 (purple) contains the TE3859 electrodes.



## Cycle 1000 Curves for 1.02 RCF



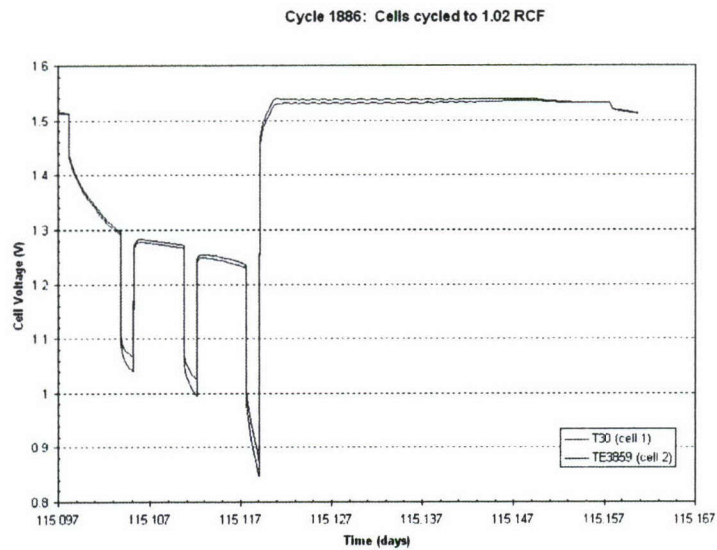
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The graph shows the voltage change in the two cells tested to a 1.02 RCF at cycle 1000. Cell 1 (blue) contains the T30 electrodes and Cell 2 (purple) contains the TE3859 electrodes.

## Cycle 1886 Curves for 1.02 RCF



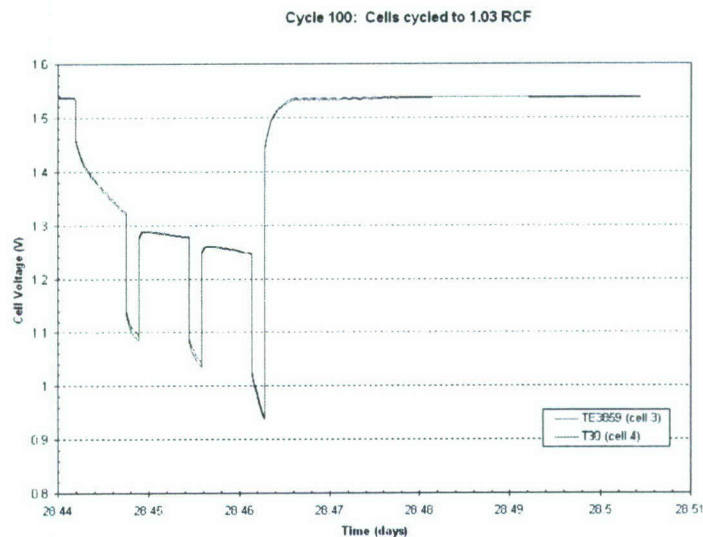
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The graph shows the voltage change in the two cells tested to a 1.02 RCF at cycle 1886. Cell 1 (blue) contains the T30 electrodes and Cell 2 (purple) contains the TE3859 electrodes.

## Cycle 100 Curves for 1.03 – 1.05 RCF



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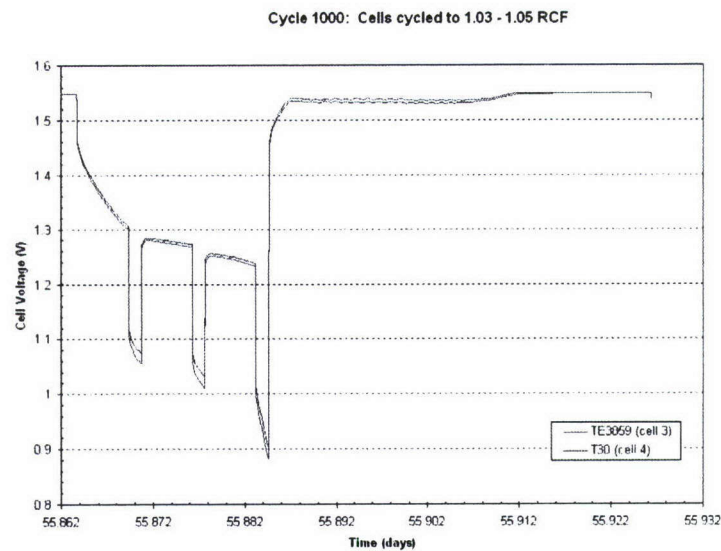
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The graph shows the voltage change in the two cells tested to an average 1.04 RCF at cycle 100. Cell 3 (green) contains the TE3859 electrodes and Cell 4 (cyan) contains the T30 electrodes.



## Cycle 1000 Curves for 1.03 – 1.05 RCF



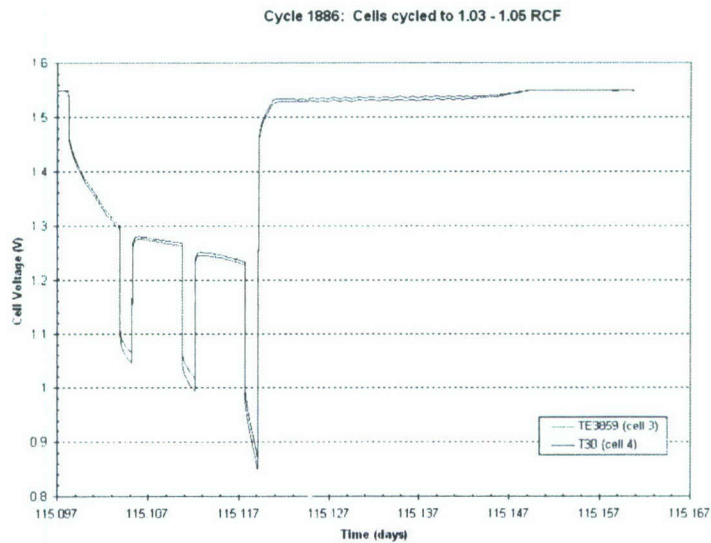
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The graph shows the voltage change in the two cells tested to an average 1.04 RCF at cycle 1000. Cell 3 (green) contains the TE3859 electrodes and Cell 4 (cyan) contains the T30 electrodes.

## Cycle 1868 Curves for 1.03 – 1.05 RCF



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The graph shows the voltage change in the two cells tested to an average 1.04 RCF at cycle 1886. Cell 3 (green) contains the TE3859 electrodes and Cell 4 (cyan) contains the T30 electrodes.

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**Space Materials Laboratory:** Evaluation and characterizations of new materials and processing techniques: metals, alloys, ceramics, polymers, thin films, and composites; development of advanced deposition processes; nondestructive evaluation, component failure analysis and reliability; structural mechanics, fracture mechanics, and stress corrosion; analysis and evaluation of materials at cryogenic and elevated temperatures; launch vehicle fluid mechanics, heat transfer and flight dynamics; aerothermodynamics; chemical and electric propulsion; environmental chemistry; combustion processes; space environment effects on materials, hardening and vulnerability assessment; contamination, thermal and structural control; lubrication and surface phenomena. Microelectromechanical systems (MEMS) for space applications; laser micromachining; laser-surface physical and chemical interactions; micropropulsion; micro- and nanosatellite mission analysis; intelligent microinstruments for monitoring space and launch system environments.

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